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Experimental Protocol for Determining Hydroxyl Radical Reaction Rate Constants for Organic Compounds: Estimation of Atmospheric Reactivity

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EXPERIMENTAL PROTOCOL FOR DETERMINING HYDROXYL RADICAL REACTION RATE CONSTANTS FOR ORGANIC COMPOUNDS
Estimation of Atmospheric Reactivity

by

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An experimental protocol for the determination at room temperature of rate constants for the reactions of hydroxyl radicals with organic chemicals in the gas phase is described in detail. This protocol provides a basis for evaluating the reactivity of organic substances which are emitted into the environment and which are consumed primarily by reaction with hydroxyl radicals.

The experimental technique is based upon monitoring the disappearance rates of the test compound and of a reference organic in irradiated methyl nitrite-NO-organic-air mixtures. Irradiations, employing blacklamps emitting in the actinic region, are carried out in ~75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite, zero to ~15 ppm; NO, ~5 ppm; test compound, ~1 ppm; reference organic, ~1 ppm. The test compound and reference organic are monitored by gas chromatography or other appropriate techniques and NO, NO_x, and O_3 by chemiluminescence instruments. Using this technique, OH radical rate constants $\geq 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} can be measured.

TABLE OF CONTENTS

Abstract		iii
List of Figures		vii
List of Tables		viii
I.	INTRODUCTION AND BACKGROUND	1
	A. Factors Affecting Reactivity	3
	B. Overall Approach Employed	5
	C. Limitations of the Experimental Technique	8
II.	GENERAL EQUIPMENT AND MATERIALS REQUIRED	11
	A. Methods for the Analyses of the Test and Reference Organics	11
	B. Ozone Monitor	12
	C. NO-NO_x Monitor	12
	D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly	13
	1. Reaction Chamber	13
	2. Injection and Sampling Port	13
	3. Heat Sealing	16
	E. Reaction Bag Cover	16
	F. Seal Reinforcement and Leak Testing	16
	G. Fluorescent Lamp Assembly	16
	H. Vacuum Gas-Handling System	18
	1. Vacuum Pumping System	18
	2. Vacuum Rack	20
	3. Pressure Gauges	20
	I. Glassware for Preparation of Methyl Nitrite	20
	J. Flowmeter	22

TABLE OF CONTENTS
(Continued)

K. Temperature Measurement 24

III. EXPERIMENTAL PROTOCOL 25

A. Operation of Gas Handling System 25

1. Start-up 25

2. Shut-down 25

3. Maintenance 26

B. Preparation of Methyl Nitrite 26

C. Experimental Procedure for the Determination of Rate Constants for Reaction with the Hydroxyl Radical 27

1. Filling the Reaction Bag 27

2. Introduction of Initial Reactants 27

a. Injection of Methyl Nitrite 27

b. Injection of NO 28

c. Injection of Test Compound and Reference Organic 30

(1) Gaseous Compounds 30

(2) Liquid Compounds 33

(3) Solid Compounds 33

3. Pre-Irradiation Analyses 36

4. Irradiation Procedure 37

5. Safety Considerations 40

D. Data Analysis 40

E. Reference Organics 41

F. Information to be Reported 41

IV. REFERENCES 45

LIST OF FIGURES

Figure Number	Title	Page
1	Construction of the Teflon Reaction Bag	14
2	Injection and Sampling Port	15
3	Fluorescent Lamp Assembly	17
4	Schematic of Gas Handling Vacuum Rack	19
5	Schematic of Glassware Assembly for Methyl Nitrite Production	21
6	Design of a Bubble Flowmeter	23
7	Attachment of Pyrex Bulbs to the Injection Port	29
8	Syringe-to-Syringe Gas Transfer	31
9	Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds	32
10	Apparatus for Introducing Solid Compounds into the Reaction Chamber	35
11	Example of Gas Chromatographic Analysis of Propene ($C_3^=$) and n-Butane (n-C_4) During a CH_3ONO/NO/Propene/n-Butane/Air Irradiation	38
12	OH Radical Concentrations During a Typical Irradiation at Full Light Intensity with an Initial Concentration of CH_3ONO of 10 ppm	39
13	Plot of Equation (V) for Several Hydrocarbons Using Ethane as the Reference Organic	42

LIST OF TABLES

Table Number	Title	Page
1	List of Several Organics for Which Accurate OH Radical Rate Constants are Available, and Which do not Photolyze	43

SECTION I

INTRODUCTION AND BACKGROUND

Volatile organic compounds, when emitted into the atmosphere in the presence of oxides of nitrogen (NO_x), can react in sunlight to contribute to the photochemical formation of ozone and other photochemical oxidants, a major air quality problem in many areas of the United States. Organic compounds are known to differ to the extent in which they contribute to ozone formation, or increase the rate of its formation. In particular, certain organics react to form ozone extremely rapidly when irradiated in the presence of NO_x, while others are essentially inert in the lower troposphere or react too slowly to affect ozone formation in the area in which they are emitted. These differences, which are referred to as the "reactivity" of the compound, need to be taken into account in assessing the impacts of emissions of different organic compounds on photochemical ozone formation.

The reactivity of organic compounds with respect to ozone formation has been defined and measured in a number of ways. These include:

- The amount of ozone produced when the organic compound is irradiated in environmental chambers in the presence of NO_x.
- The rate of NO oxidation observed in such environmental chamber irradiations [NO oxidation in organic-NO_x-air irradiations is directly related to ozone formation, as discussed in detail elsewhere (Bufalini et al. 1976, Finlayson-Pitts and Pitts 1977, Atkinson and Lloyd 1984)].
- The rate of removal of the organic compound in environmental chamber irradiations.
- The rate at which the organic compound reacts with hydroxyl radicals.

The first three of these approaches to defining and measuring reactivity involve the use of environmental chamber irradiations, which have served as the basis of most past studies of ozone forming reactivity. However, environmental chamber irradiations are subject to a number of problems, for example "dirty chamber" effects, and this experimental technique has been shown to be particularly unsatisfactory in determining the ozone-forming reactivities of slowly reacting compounds

(Bufalini et al. 1977). Since an important question concerning the reactivity of organic compounds involves differentiating between organic compounds considered to be unreactive and those which are reactive, this is a serious limitation.

Some of the problems with defining and measuring reactivity using smog chamber experiments can be circumvented by defining reactivity in terms of the rates at which the organic compounds react with the hydroxyl (OH) radical. This involves, in general, far fewer experimental problems, since for most compounds these rate constants can be measured to a fair degree of accuracy by a number of techniques, some of which are suitable for slowly reacting compounds (Atkinson et al. 1979, Atkinson 1985). This definition of reactivity assumes that reaction with the hydroxyl radical is the major atmospheric loss process for the organic compound being tested, and that the rate at which the compound reacts in the atmosphere is the most important factor in influencing its overall reactivity. As discussed below in section I.A, these assumptions are not always correct. Thus some organic compounds are consumed to a significant extent in the atmosphere by other reaction pathways, and in certain cases factors other than the initial OH radical reaction rates can have a significant influence on their overall reactivity. However, for a majority of the organics which are currently emitted in significant quantities into the atmosphere and whose atmospheric reactions have been studied, reaction with OH radicals is indeed the major removal process (Atkinson et al. 1979, Atkinson 1985). Furthermore after reaction with OH radicals, these compounds generally tend to form intermediates which cause ozone formation in the presence of NO_x and sunlight (Bufalini et al. 1976, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson et al. 1979, Atkinson and Lloyd 1984).

In this document, a procedure is described for measurement of the room temperature rate constants for the reaction of organic compounds with OH radicals, in order to assess their atmospheric reactivity. This procedure is based on the relative rate technique previously developed and tested by Pitts et al. (1982), and is among the simplest of the techniques which can be accurately applied for this purpose. An overview of this procedure is given in section I.B below. However, this procedure has a number of limitations, both with respect to the concept of defining ozone-

forming reactivity solely in terms of hydroxyl radical rate constants, and with respect to experimental problems with the technique when applied to measuring OH radical rate constants for certain classes of organic compounds. The potential experimental limitations are discussed in section I.C. Despite these limitations, however, the procedure described in this document can be usefully employed as a preliminary screening method for assessing the ozone-forming reactivity for many classes of organic compounds.

A. Factors Affecting Reactivity

The extent to which an organic compound contributes to ozone formation is influenced by a number of factors, and in principle all of these should be taken into account in assessing its reactivity. These factors are:

- How rapidly the organic compound reacts in the atmosphere.
- The amount of ozone formed (or NO oxidized) when a given amount of the organic compound reacts.
- The extent to which the reactions of the organic compound enhance or suppress radical levels, which affects the rates of reaction of all organic compounds present in that particular air mass.
- The extent to which the reactions of the organic compound contribute to the consumption of NO_x; this in turn affects ozone formation since this is only significant when NO_x is present.

The chemical loss rate of an organic compound under atmospheric conditions is an important factor with regards to its ozone forming potential. This is especially so for the slower reacting organic compounds, since if they do not react they can have no effect on ozone formation. Thus the reaction rate under atmospheric conditions is an important factor with regard to whether or not an organic compound can be considered to be reactive or unreactive with respect to O_3 formation. As indicated above, the experimental protocol described in this document is concerned with measuring this aspect of reactivity.

However, once a compound emitted into the atmosphere has undergone reaction, mechanistic factors, in particular those listed above, determine the specific influence of the organic compound on ozone formation. An important factor is whether the reactions of the compound suppress or

enhance radical levels. Since the formation of photochemical smog is primarily a radical chain process, radical inhibitors or initiators have an important effect on the overall reactions in the system, including the rates at which other organic compounds react to cause ozone formation. Certain compounds, such as toluene and the xylenes (Atkinson et al. 1980, Killus and Whitten 1982), and furan and pyrrole (Carter et al. 1984a) tend to be more reactive in NO_x-air irradiations than expected from their OH radical rate constants. This is attributed to the formation of radical initiators in their atmospheric photooxidation reactions pathway. Certain chlorinated compounds, such as tetrachloroethene, also tend to be more reactive than expected, due to radical initiation via the formation of chlorine atoms.

A number of other organic compounds which have been studied have been shown to have significant radical (as well as NO_x) sinks, and thus act as inhibitors for ozone formation. Examples of such compounds are benzaldehyde (Atkinson et al. 1980), the cresols (Atkinson et al. 1980), amines (Lindley et al. 1979), and the higher alkanes (Atkinson and Lloyd 1984). For these compounds, ozone formation in their NO_x-air photooxidation is markedly less than expected based solely on their rates of reaction with the OH radical. Furthermore, addition of these compounds to photochemical smog systems can cause a reduction, rather than an enhancement, of ozone formation, leading to the concept of "negative" reactivity. This possibility of negative reactivity is not taken into account when reactivity is defined solely in terms of OH radical reaction rates. However, for compounds which are not radical inhibitors the rates at which they react can serve as a semi-quantitative estimate of their ozone-forming reactivity.

The protocol described in this document is based on the assumption that organic compounds are consumed in the atmosphere primarily by reaction with the hydroxyl radical. However, certain organic compounds can react in the atmosphere in a number of other ways, and environmental chamber and laboratory studies have shown examples for which one or more of the following removal processes are of significance:

- Reaction with ozone.
- Direct photolysis.
- Reaction with the nitrate (NO_3) radical.
- Reaction with nitric acid (HNO_3).

For example, reaction with ozone is an important atmospheric sink for the alkenes and other unsaturated compounds, and may be the dominant removal process for the hydrazines (Tuazon et al. 1981, Atkinson and Carter 1984). Direct photolysis can be an important removal process for carbonyl compounds and is the dominant atmospheric sink for most nitrites and nitroso compounds. Reaction with the NO_3 radical has been shown to be a dominant sink for the reactions of phenolic compounds in atmospheres polluted with both ozone and NO_x (Carter et al. 1981, Atkinson et al. 1984), and has been more recently shown to be an important atmospheric sink for a number of other compounds, examples being furan, thiophene, and pyrrole (Atkinson et al. 1985), the monoterpenes, and dimethyl sulfide (Winer et al. 1984). For basic compounds such as the amines and pyridine, reaction with nitric acid is possibly an important removal process in polluted atmospheres, where significant quantities of nitric acid may be present.

However, as indicated above, for most organic compounds reaction with the hydroxyl radical is the dominant homogeneous atmospheric removal process. Thus, for example, reaction with hydroxyl radicals is the major atmospheric removal process for the alkanes, aromatic hydrocarbons, simple saturated alcohols and ethers, saturated halogenated organics and many other classes of compounds (Atkinson 1985). These constitute a majority of the organic compounds which are emitted in significant quantities into the atmosphere and whose atmospheric reaction rates are known or can be estimated. For compounds such as these, the application of this protocol can give a reasonably reliable indication of atmospheric removal rates, and a basis for estimating their reactivity with respect to ozone formation.

B. Overall Approach Employed

As indicated above, the experimental procedure described in this document consists of measuring the relative rate constants for the reaction of volatile organic compounds with the hydroxyl radical. This

procedure also yields information regarding the photolysis rate constants for these organic compounds, though a protocol specifically designed for that purpose is described in detail elsewhere (Carter et al. 1984b). The specific experimental procedure for determining OH radical rate constants is based on measuring the relative rates of disappearance of the test compound and a reference organic in irradiated methyl nitrite (CH_3ONO)-NO-organic-air mixtures. If both the test and reference organics are consumed primarily by reaction with OH radicals, then the data can be analyzed to yield the ratio of OH radical rate constants for those two compounds. Using the known rate constant for the reaction of OH radicals with the reference organic, the rate constant for the test compound can then be determined.

The photolysis of CH_3ONO in air is a convenient method to generate high concentrations of OH radicals by the following reactions:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In the presence of added organics, the OH radicals react with these organics:

$$OH + \text{test compound} \rightarrow \text{products} \qquad (1)$$

$$OH + \text{reference organic} \rightarrow \text{products} \qquad (2)$$

In addition, the test compound may also photolyze, react with ozone and/or react with the NO_3 radical:

$$\text{test compound} + h\nu \rightarrow \text{products} \qquad (3)$$

$$\text{test compound} + O_3 \rightarrow \text{products} \qquad (4)$$

$$\text{test compound} + NO_3 \rightarrow \text{products} \qquad (5)$$

Excess NO is included in the reaction mixture in order to minimize the importance of reactions (4) and (5), since O_3 and NO_3 both react rapidly with NO:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO + NO_3 \rightarrow 2\ NO_2$$

If the organics are lost only by reaction with OH radicals and, for the test compound, photolysis, then

$$-d[\text{test compound}]/dt = k_1[OH][\text{test compound}] + k_3\ [\text{test compound}] \quad (I)$$

$$-d[\text{reference organic}]/dt = k_2[OH]\ [\text{reference organic}] \quad (II)$$

where k_1 and k_2 are the OH radical rate constants for reactions (1) and (2), respectively, and k_3 is the photolysis rate constant. Hence

$$d\ln[\text{test compound}]/dt = k_1[OH] + k_3 \quad (III)$$

and

$$d\ln[\text{reference organic}]/dt = k_2[OH] \quad (IV)$$

Elimination of the OH radical concentration and integration leads to

$$\frac{1}{(t-t_o)} \ln\left\{\frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t}\right\} = k_3 + \frac{k_1}{k_2(t-t_o)} \ln\left\{\frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}\right\} \quad (V)$$

where $[\text{test compound}]_{t_o}$ and $[\text{reference organic}]_{t_o}$ are the concentrations of the test compound and the reference organic, respectively, at time t_o, and $[\text{test compound}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time t. Note that equation (V) is valid even if the OH radical concentration varies with time.

Hence a plot of $(t-t_o)^{-1}\ \ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $(t-t_o)^{-1}\ \ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 and intercept k_3. Knowing k_2, the

rate constant k_1 may then be derived. If the test compound does not photolyze (i.e., $k_3 = 0$), then equation (V) can be simplified to yield:

$$\ln\left\{\frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t}\right\} = \frac{k_1}{k_2} \ln\left\{\frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}\right\} \qquad \text{(VI)}$$

and a plot of $\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $\ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 with a zero intercept.

The concentrations of the test compound and the reference organic are monitored before and during irradiation of the CH_3ONO-NO-test compound-reference organic-air mixtures by gas chromatography or by other suitable analytical techniques. Hence the lower limit to k_1 that can be determined is set by the precision of the analyses, but is expected to be of the order of $\lesssim 3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1} under optimum conditions.

C. Limitations of the Experimental Technique

The general technique outlined above and described in detail in the following sections has been developed to provide rate constant ratios for the reactions of OH radicals with a wide variety of organic compounds, with an experimental precision in many cases exceeding that possible with current absolute techniques (see Atkinson 1985 for examples and a discussion of the current rate constant measurement techniques). However, there are certain classes of compounds for which this technique probably cannot be successfully applied, at least not without significant modifications. Examples of such classes are as follow:

- Compounds which react with OH radicals with rate constants lower than $\sim 3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. This is not a serious limitation for the purpose of estimating their ozone-forming reactivity since compounds which react slower than this are considered to be unreactive. (An OH radical rate constant of 3×10^{-13} cm^3 molecule^{-1} sec^{-1} corresponds to an atmospheric lifetime of >80 days, assuming a global 24-hour annual average OH radical concentration of $\sim 5 \times 10^5$ cm^{-3}.)

• Compounds for which no reliable and precise technique exists for measurement of their concentration in air. The measurement technique should be sensitive enough to monitor the organic compound at part-per-million (ppm) levels. This protocol presumes that such a suitable analytical technique for the test compound and the appropriate reference organic exists and is available at the laboratory carrying out this protocol. However, since this technique is based on the measurement of relative decay rates, it is not necessary to be able to measure the absolute concentrations. Thus, this protocol can be applied even if no reliable technique exists for the measurement of absolute concentrations of the test organic.

• Compounds which have insufficient volatility to be introduced into the gas phase at high enough concentrations to be measured. It should be noted, however, that extremely non-volatile compounds can be considered to be unreactive, and this protocol thus need not be applied to such compounds.

• Compounds which tend to be absorbed onto the walls of the reaction vessel. This is evidenced by (a) the levels of the compound monitored in the gas phase in the reactor being less than those expected from the quantity injected, (b) by the measured concentrations of the compound decreasing with time in the reaction chamber prior to the irradiation, or (c) by the gas phase concentration of the organic compound increasing after the lights are turned on. Tests for determining whether or not any of these occur must be carried out prior to conducting this protocol. Moderate wall adsorption problems may not be too severe a limitation providing that the organic compound reacts sufficiently rapidly that the the rate of its consumption due to chemical reaction when the lights are on is more rapid than the rate of wall adsorption/desorption. However, the kinetic data obtained will necessarily be more uncertain.

• Compounds which photolyze so rapidly that their photolysis is a more important loss process in CH_3ONO-air photolysis systems than is their reaction with OH radicals. This will be the case for compounds whose photolysis rates in sunlight or blacklight irradiation are comparable to or exceed that of methyl nitrite and can be readily checked by carrying out the experimental protocol as described below. For such compounds, an alternate procedure based on using the hydrazine + ozone reaction as a

dark OH radical source can be applied -- provided that they do not react with hydrazine or ozone (Tuazon et al. 1983). However, if a compound photolyzes this rapidly, then photolysis will be its dominant atmospheric removal pathway and its OH radical rate constant will not be an important factor in determining its reactivity.

- Compounds whose photooxidation mechanism involves the release of chlorine (or possibly fluorine) atoms, since these may contribute to the consumption of the test compound and the reference organic. If this is suspected to be the case, ethane, propane or some other suitable compound whose Cl atom/OH radical rate constant ratio is significantly higher than that for the reference organic can be included in the reaction mixture at sufficiently high levels that the majority of the chlorine atoms reacts with it. (Chlorine atoms are a more reactive and thus less discriminating species than OH radicals in terms of reacting with most organics, and thus the Cl atom/OH rate constant ratio will be relatively higher for less reactive compounds.) The modifications to the protocol for such cases is beyond the scope of this document.

- Compounds which react with nitric acid vapor. Nitric acid is formed as a product in irradiated CH_3ONO-NO systems from the reaction with OH radicals with NO_2, and may thus contribute to the consumption of the test organic if the test organic reacts with HNO_3. Tests can be carried out to determine whether this is the case, especially if the compound is known to be basic in nature.

In general, if the results of this protocol appear to be anomalous, as indicated, for example, by non-linear plots of equation (V), then the possibility of these or other experimental problems should be investigated. In some cases, such problems may be anticipated based on our knowledge of the chemistry of the class of compounds being investigated. In these cases, appropriate tests should be carried out to assure the validity of the protocol.

SECTION II

GENERAL EQUIPMENT AND MATERIALS REQUIRED

To determine rate constants for the reaction of OH radicals with organic compounds using the method outlined above, the following major pieces of equipment are needed:

- A gas chromatograph or other analytical equipment required for precision gas phase analyses of the test and reference organics.
- An ozone monitor equipped with a filter to remove particulates.
- An NO-NO_x monitor.
- A Teflon bag or chamber in which the reaction can be carried out.
- An arrangement of fluorescent lamps.
- A greaseless high vacuum rack.

The specific requirements and recommendations for these items of equipment are discussed below.

A. Methods for the Analyses of the Test and Reference Organics

While it can be seen [equations (V) and (VI)] that only relative measurements of the test and reference organic concentration are necessary, it is recommended that quantitative analyses be carried out. For the development of this experimental protocol, gas chromatography was used to analyze the test and reference organics. However, any analysis technique that is specific for the test and reference organics, can monitor these compounds at the concentrations necessary for this protocol, i.e., ~0.1-1 part-per-million (ppm), and which samples over a time period short compared to the irradiation times can in principle be used. (For example, mass spectrometry, combined gas chromatography-mass spectrometry or in-situ spectroscopic techniques can also be employed). Since sampling for the test and reference organics must be carried out simultaneously for this protocol, the same technique of choice should be used for both species. It is taken for granted that quantitative analyses of the test compound by such techniques will have been developed at the laboratory conducting this protocol. Hence, this aspect of the protocol is considered beyond the scope of this document.

For the reference organics which are recommended for use here (see Section III), the gas chromatographic columns and conditions used in the development of this protocol were as follows (Pitts et al. 1979):

n-Butane, cyclohexane, isoprene and 2-methyl-2-butene (and other C_4 through C_{10} n-alkanes) were analyzed using a 20-ft x 1/8-in. stainless steel column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb G, operated at 333 K. The N_2 carrier gas flow was 50 cm^3 min^{-1}, and a 3.0 cm^3 gas sample loop was used.

Propene, n-butane (and other $>C_3$ alkanes and alkenes) were analyzed using a 36-ft x 1/8-in. stainless steel column of 10% 2,4-dimethylsulfolane on C-22 firebrick (100/120 mesh) operated at 273 K. The N_2 carrier gas flow was 80 cm^3 min^{-1} and a 2.0 cm^3 gas sampling loop was used.

For all of these analytical systems, no preconcentration was necessary and flame ionization detection was employed in all uses.

B. Ozone Monitor

It is necessary to monitor ozone when carrying out this protocol in order to assure that it is not being formed at sufficiently high concentrations to contribute to the consumption of organics which might react with ozone or NO_3 radicals. A chemiluminescence ozone analyzer is recommended for this protocol since the ozone analyzers utilizing ultraviolet absorption tend to respond not only to ozone but also to some chemicals which absorb radiation at 253.7 nm [e.g., the cresols (Atkinson et al. 1980)]. This may include some of the OH radical reaction products. The ozone analyzer used will have an optimum sampling rate specified by the manufacturer; any sampling rate less than ~2 liters min^{-1} is acceptable. The ozone analyzer should be calibrated according to the manufacturer's specifications.

C. $NO-NO_x$ Monitor

A chemiluminescence $NO-NO_x$ monitor (using the ozone-nitric oxide reaction) is recommended for this protocol. The monitor should be calibrated according to the manufacturer's specifications. It should be noted that the NO_2 and NO_x readings on such monitors are subject to positive interferences by organic nitrates and other nitrogenous species (Winer et al. 1974), including methyl nitrite and the methyl nitrate

formed as a product in the methyl nitrite-NO irradiation system. Thus these readings can only be taken to be upper limits to the true NO_2 or NO_x levels. This will be particularly true if the test organic or reference compound are nitrogenous compounds, or if they tend to form, as is the case for the higher alkanes, organic nitrates in their NO_x-air photooxidation reactions. Fortunately, accurate NO_2 measurements are not required for this protocol. The NO data are unaffected by this interference.

D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly

1. Reaction Chamber

A simple, yet totally adequate, reaction chamber consists of an ~75-liter FEP Teflon cylindrical reaction bag (FEP Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.), formed from three pieces of 2 mil FEP Teflon. A diagram showing the construction of such a reactor is shown in Figure 1. The two end pieces are ~45 cm in diameter with an ~45 cm wide, ~140 cm long piece forming the cylinder. Teflon is the preferred material for construction of the reaction chamber because of its general inertness to ozone and its lack of hydrocarbon offgassing.

2. Injection and Sampling Port

Prior to heat sealing the Teflon chamber sides, a port for injection of the reactants and for sampling must be fitted. This sampling and injection port should be constructed of TFE Teflon nuts and bolts with the appropriate Swagelok stainless steel fittings. (Swagelok is a registered trade name of Crawford Fitting Company.)

Figure 2 shows the design of the sampling and injection port used in this protocol. The port consists of a 2-3" long hollow bolt of Teflon (A), machined on the exterior surface with threads. The interior hold (B) is 1/4" in diameter and an ~8" long 1/4" o.d. Teflon tube is inserted as shown. Two Teflon nuts (D) then screw over the bolt (A), one on the inside of the bag, the other on the outside. Large Teflon washers (E) are placed between the Teflon bag and the nuts (D), thus enabling the nuts to be tightened without twisting or stretching the Teflon bag. The 1/4" o.d. Teflon tube is connected outside the reaction bag to a glass-Teflon stopcock.

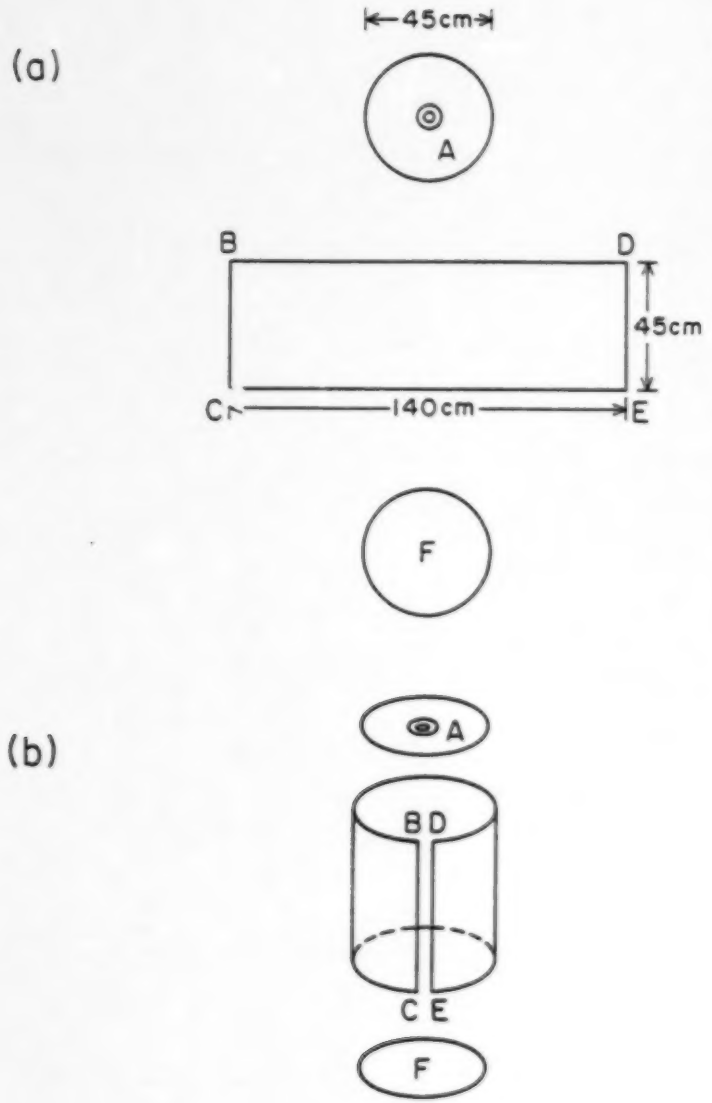
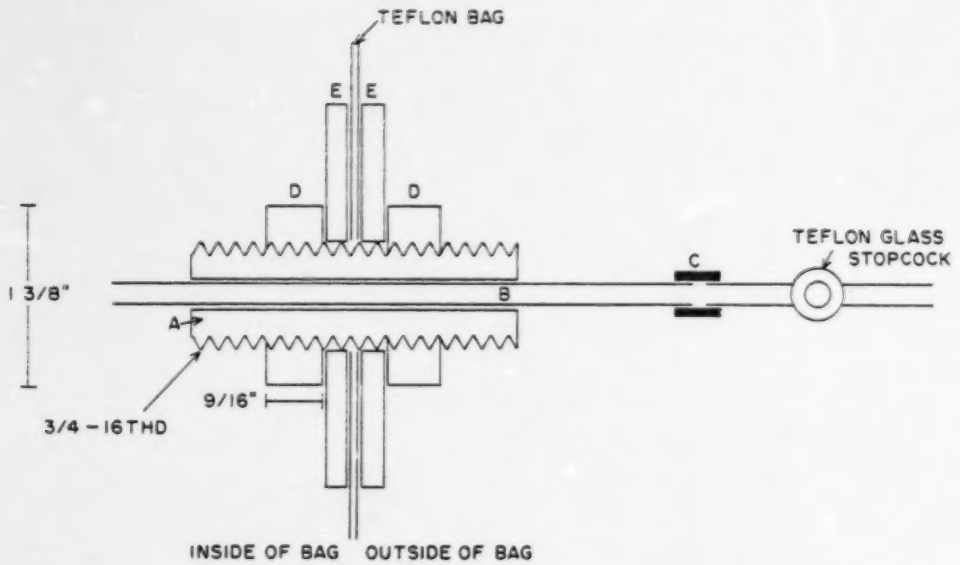


Figure 1. Construction of the Teflon Reaction Bag



A HOLLOW TEFLON BOLT
B 1/4" O.D. TEFLON TUBE INSERTED THROUGH 1/4" DIAMETER HOLE
C TYGON TUBING
D TEFLON NUTS
E TEFLON WASHERS

Figure 2. Injection and Sampling Port

3. Heat Sealing

The Teflon port is first assembled on one of the ends of the chamber by tightening the Teflon nuts, as detailed above and as shown in Figures 1 and 2. The hole in the Teflon sheet through which the Teflon bolt (A) fits can be conveniently made using a cork borer. The sides of the resulting cylindrical bag are sealed together with a 500 watt thermal impulse heat-sealer. It will probably be necessary to carry out preliminary testing of this heat-sealing technique using scrap pieces of Teflon to obtain a heat setting that yields a strong seal.

E. Reaction Bag Cover

An opaque cover is necessary in order to avoid illumination of the reaction chamber and hence possible photolysis of the methyl nitrite or the test compound being studied before the timed experiment begins. A large opaque plastic sheet functions well.

F. Seal Reinforcement and Leak Testing

The heat-sealed sides can be further protected from leaks by covering the heat-sealed seams with green Mylar tape. After the bag is constructed it should be tested for obvious leakage by filling with pure air (ultra-high purity) to capacity (not excessively so as to split the seams) and then allowing the inflated bag, with the stopcock closed, to sit for one or two hours. After this period of time, the amount of deflation can be visually estimated. A certain amount of air will have permeated through the Teflon, but the bag should still be largely filled, and no obvious leaks should result from applying a small amount of pressure to the bag. The seams should be carefully examined for splits or tears, and, if any are found, they should be resealed (probably at a lower heat setting) and more Mylar tape applied to reinforce the seams.

G. Fluorescent Lamp Assembly

The fluorescent lamp assembly used in the development of this protocol is shown schematically in Figure 3. It consists of a circular array of 24 15-watt blacklights (GE F15T8-BL15) mounted in a cylindrical frame constructed of aluminum. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on the same

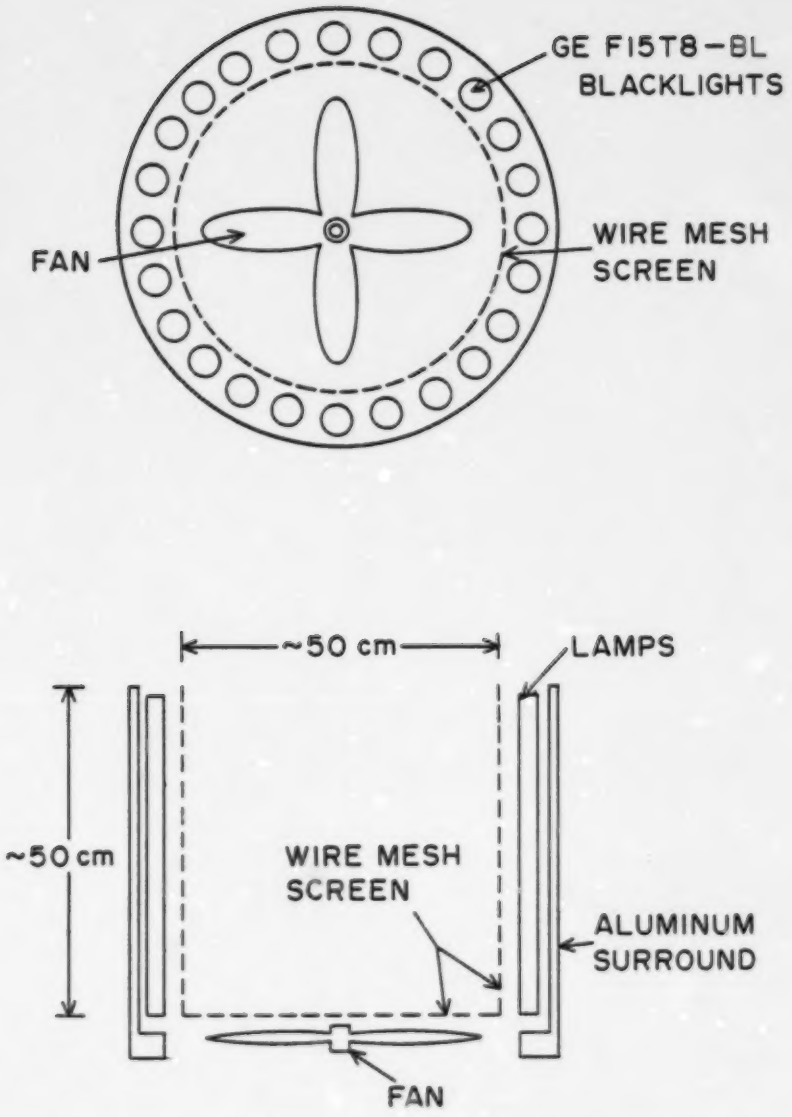


Figure 3. Fluorescent Lamp Assembly

circuit. This allows the use of three differing light intensities. In the bottom of the assembly is a fan which circulates a large volume of air to minimize heating of the reaction chamber. A cylindrical wire mesh screen inside the lamp ring (Figure 3) keeps the reaction bag from contact with the lamps or the fan.

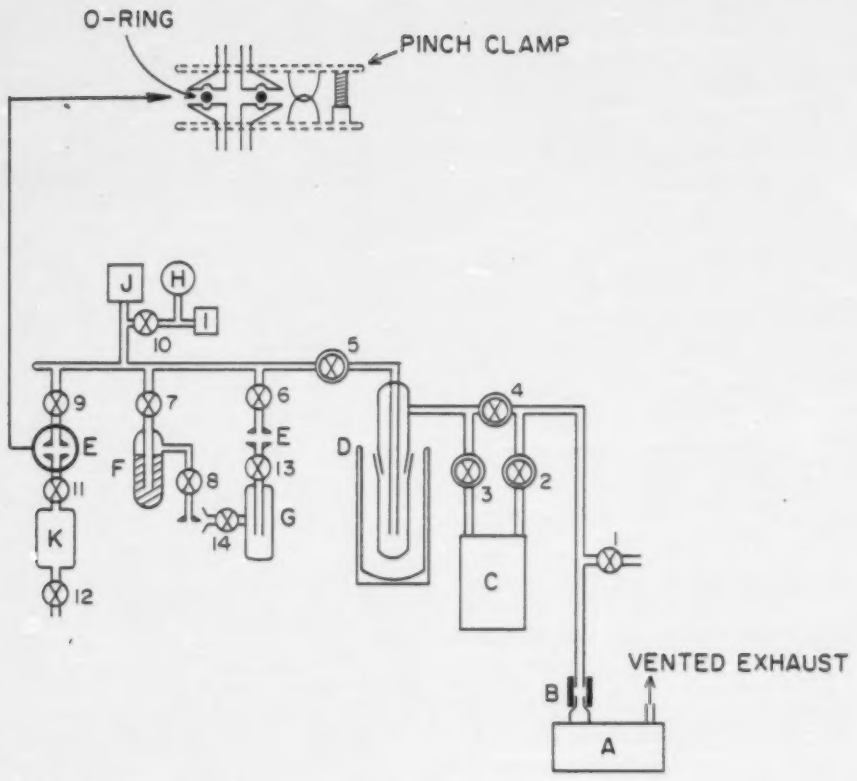
H. Vacuum Gas-Handling System

A gas-handling system is necessary for the preparation and gas handling of methyl nitrite and may also be useful for the preparation and purification of the test or reference compounds. A suitable system is shown diagramatically in Figure 4. Such a system should be constructed from Pyrex, since the use of other materials, such as various metals, can lead to wall adsorption problems. The components of such a gas handling system are discussed below.

1. Vacuum Pumping System

Two pumps, working in tandem, are necessary to provide good vacuum, i.e., pressures $\lesssim 10^{-5}$ torr. The forepump (A) must be capable of achieving pressures $\lesssim 0.05$ torr. A rotary pump such as a Welch Model 1402 Duo-Seal or equivalent is recommended for this purpose. The forepump is attached to the rest of the vacuum system by heavy-walled rubber vacuum tubing (B), which also serves to damp-out transmission of vibrations to the vacuum line. The exhaust from this pump should be vented into a hood. The second, and high-vacuum, pump required is a multistage oil diffusion pump (C), a CVC (Consolidated Vacuum Corporation) VMF-10 or VMF-20 or equivalent being suitable. The working fluid should be a silicone oil (e.g., Dow-Corning DC703) since it is less susceptible to destructive oxidation should the system be inadvertently opened to air while the diffusion pump is still hot. The diffusion pump fluid must have a room temperature vapor pressure of $\lesssim 10^{-6}$ torr.

The pumping system must be equipped with a trap (D) cooled by liquid nitrogen (i.e., at 77 K) to reduce pump oil contamination and back-streaming. The cone and socket portions of this trap (Figure 4) may be conveniently sealed using Apiezon W wax (which requires gentle heating to apply).



A ROTARY PUMP
B RUBBER TUBING (THICK WALLED)
C DIFFUSION PUMP
D TRAP AT LIQUID NITROGEN TEMPERATURE
E #7 OR 9 O-RING JOINTS
F MOLECULAR SIEVE 4A TRAP
G CH_3ONO TRAP
H THERMOCOUPLE GAUGE
I IONIZATION GAUGE
J CAPACITANCE MANOMETER
K ~500cm^3 PYREX BULB

⊗ 0-4 OR 0-5 mm STOPCOCKS

⊗ 0-8 OR 0-10 mm STOPCOCKS

Figure 4. Schematic of Gas Handling Vacuum Rack

2. Vacuum Rack

A suitable assembly of the vacuum rack is shown in Figure 4. The stopcocks should be of Teflon with Viton "o"-rings, such as the Kontes #K-826500 or K-826510 series. The "o"-ring joints (#7 or #9 size are suitable) must be chosen to be compatible with those on the methyl nitrite trap (G). These "o"-ring joints should be clamped by pinch clamps with a screw lock device (Thomas #18A, available from VWR Scientific, Inc., for example).

3. Pressure Gauges

Two, or preferably three, pressure gauges are required:

(a) An ionization gauge to measure high vacuum, i.e., pressures $\lesssim 10^{-3}$ torr, to verify that the vacuum system is operating correctly and that there are no leaks.

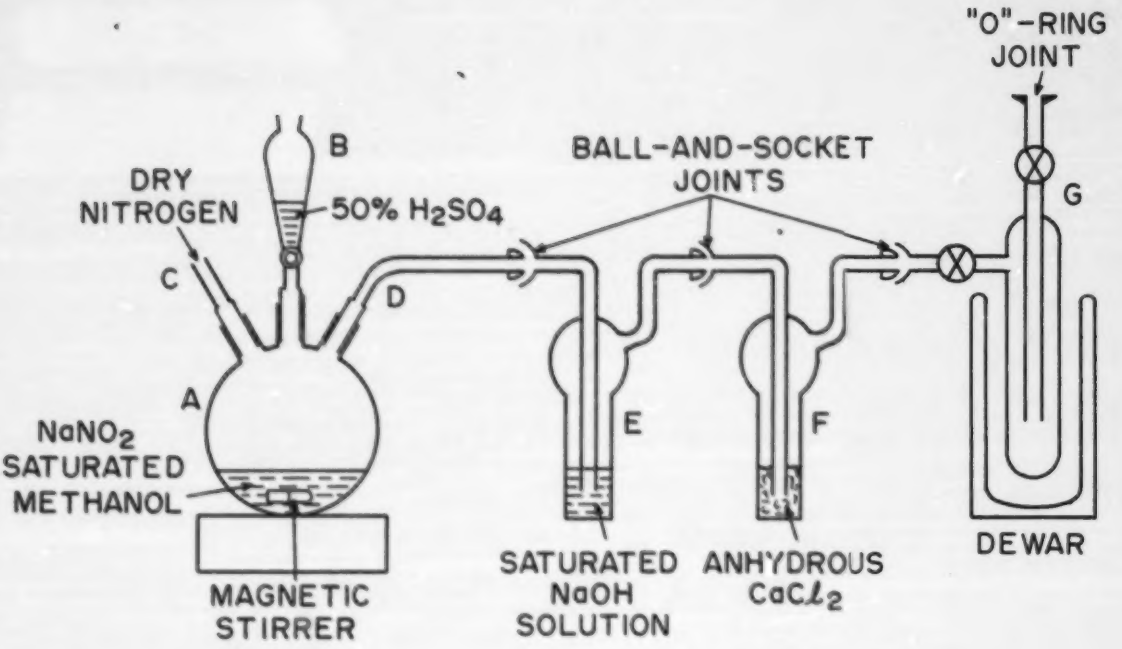
(b) If available, a thermocouple gauge is desirable to monitor, on a semi-quantitative basis, pressures in the range $\sim 10^{-3}$ to 1 torr. This gauge is used to monitor the pressures in the gas handling system prior to turning on either the diffusion pump (which requires pressures of $\lesssim 0.1$ torr) or the ionization gauge. A convenient pressure monitoring system which includes both these gauges is the CVC Products, Inc., Model GIC-300A ionization gauge with associated thermocouples, or equivalent.

(c) The third pressure gauge is needed to accurately monitor pressures of methyl nitrite during its preparation in the range ~0.01 to 760 torr. For this purpose a capacitance manometer should be used, such as an MKS Baratron 310 BHS-1000 with an associated 170-6C electronics unit and a digital readout (this particular system has a usable range of <0.1 to 1000 torr). While these vacuum gauges exhibit a slow zero drift, they can be readily re-zeroed using the ionization gauge, i.e., when the ionization gauge reads $\lesssim 10^{-3}$ torr.

I. Glassware for Preparation of Methyl Nitrite

The glassware required for the preparation of methyl nitrite is shown in Figure 5.

- A 300-mℓ three-necked flask
- A 250-mℓ separating funnel with an appropriate ground glass joint.
- Two bubblers fitted with 12/5 ball and socket joints.



A 300ml THREE-NECKED ROUND BOTTOMED FLASK

B 250ml SEPARATORY FUNNEL

C DRY NITROGEN INLET

D NITROGEN-CH_3ONO OUTLET

E,F BUBBLERS

G TRAP

⊗ HIGH-VACUUM GREASE-LESS STOPCOCKS (0-4 OR 0-5mm)

◎ TEFLON STOPCOCK

Figure 5. Schematic of Glassware Assembly for Methyl Nitrite Production

- A Pyrex trap fitted with high vacuum greaseless Teflon stopcocks, a ball and socket joint, and an "o"-ring joint (Figure 5).
- Other associated glass fittings as shown in Figure 5.

J. Flowmeter

A rotameter (Matheson 604 flowmeter or its equivalent) with a flow range of ~1 to 10 liter min^{-1} is an effective means for controlling and monitoring the rate of fill of the reaction chamber. When not flushing a test compound into the chamber, the fill rate may be relatively rapid, i.e., ~7-10 liter min^{-1}. However, when a liquid or a solid needs to be introduced into the chamber, this is accomplished by flushing the compound of interest from an ~1-liter bulb or for a solid, from a pyrex tube (1/4 in o.d) packed with the solid with pure air into the bag at a lower flow rate, i.e., ~3 liter min^{-1}. At high flow rates the test compound may not completely vaporize before the bag is filled). A slower flow rate still may be useful for particularly low volatility compounds, though use of a heat gun will aid vaporization in these cases.

Rotameters are often accompanied by a manufacturer's calibration curve for air. Although this calibration curve could be used, it is advisable to determine accurately the flow rate calibration curve. Flow rates should be determined at several (at least five) rotameter settings covering the flow rates to be used (i.e., 1-10 liter min^{-1}). At these flow rates a wet test meter (Precision Scientific Model No. 63126 or equivalent) is preferable, although a 1000 cm^3 or (preferably) a 2000 cm^3 bubble flowmeter can also be used. If neither a wet test meter nor a bubble flowmeter is available, a bubble flowmeter can be readily constructed by narrowing one end of a large glass tube (~5 cm diameter), as shown in Figure 6.

By adding water from a 100 cm^3 volumetric flask which has been filled to the mark and noting the water level after each successive addition of water, indelible lines can be drawn on the glass of the flowmeter at intervals of 100 cm^3, with the flowmeter in a vertical position, and, as shown in Figure 6, the zero line being above the narrow portion of the flowmeter. To the narrow end of the glass tube a glass "T" is attached by Tygon tubing, and the lower arm is enclosed with a disposable pipette

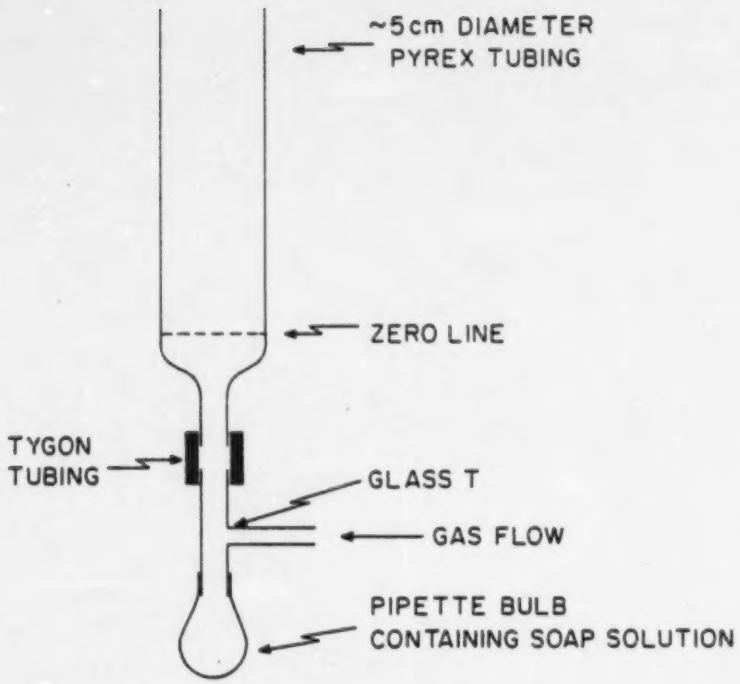


Figure 6. Design of a Bubble Flowmeter

bulb. A Tygon tubing line which carries the gas is attached to the other arm of the "T".

The pure air should first be passed through the rotameter, and its setting adjusted and noted. When using a wet test meter, measure the time, t, for a change of volume, V. For a bubble flowmeter, first squeeze the pipette bulb (containing soap solution, e.g., SNOOP [a registered trade name of Nupro Company]) to start a soap bubble and again measure the time, t, for the soap bubble to pass through a known volume V (the sidewalls of the bubble flowmeter should be well washed with soap solution so that bubbles will not break). For both types of flowmeters at least three repeat readings should be taken at each rotameter setting. The volumes V should be such that the corresponding times t exceed 10 seconds. The flow rate F (in liter min^{-1}) is given by

$$F = \frac{V(cm^3) \times 60}{t(sec) \times 1000} \qquad \text{(VII)}$$

K. Temperature Measurement

A thermometer or thermocouple suitable for measuring the temperature in the immediate vicinity of the reaction bag is required. A simple thermometer covering the range 0 to 100 C, with an accuracy of ±0.1 C, is suitable.

SECTION III

EXPERIMENTAL PROTOCOL

A. Operation of Gas Handling System

The gas handling system is required for the synthesis of the methyl nitrite and its preparation for injection into the reactor for the rate constant determinations. It can also be used for the injection of the test or reference organics, if desired. The start-up, shut-down and maintenance of this system is described in this section.

1. Start-Up

The following describes briefly the typical start-up operation of the vacuum gas handling system (Figure 4).

(1) With all stopcocks closed, switch on rotary pump (A), then open stopcock 4 and place a Dewar of liquid nitrogen around trap D.

(2) Open stopcock 10 and monitor the pressure using the thermocouple gauge (H). If the pressure is >0.1 torr, then open stopcock 5. When the pressure as read by the thermocouple gauge (H) is <0.1 torr, turn on the diffusion pump (C), open stopcocks 2 and 3 and close 4. When the diffusion pump has reached operating temperature, the pressure in the vacuum manifold should be $<10^{-5}$ torr as read by the ionization gauge (I). At this point the capacitance manometer (J) can be zeroed. The ionization gauge (I) should only be used when, as indicated by the thermocouple gauge (H), the pressure is $\lesssim 10^{-3}$ torr.

(3) The ~500-ml Pyrex bulb cell (K) can now be evacuated by opening stopcocks 9 and 11. If the bulb is at a substantial pressure, then prior to opening these stopcocks, the diffusion pump should not, if possible, be exposed to pressures >0.1 torr to avoid degradation of the pump oil. Rather, in this situation bulb (K) should be evacuated to <0.1 torr using the rotary pump alone, i.e., with stopcocks 2 and 3 closed and 4 open.

2. Shut-Down

The gas-handling system can be shut down by the following procedure: (a) close stopcocks 5 to 11, (b) switch off the diffusion pump, (c) when the diffusion pump is cool, close stopcocks 2 and 3 and open 4, (d) remove the Dewar from trap (D) and allow it to warm up, (e) then close stopcock 4 and switch off the rotary pump. Stopcock 1 should then be opened, to prevent back-up of the rotary pump oil. With this

procedure, the vacuum manifold, the trap (D) and the diffusion pump are left under vacuum.

3. Maintenance

If the vacuum system, including the bulb (K) [i.e., all stopcocks open except stopcocks 1, 4, 6 and 7] does not pump down to $<10^{-4}$ torr, then either a leak or contaminant offgassing problem is present. Closing stopcocks 11, then 9, will give indications as to the region of the problem, i.e., if, on closing stopcock 9 the pressure drops, then there may be a leak around the "o"-ring joint on the ~500 mℓ bulb (K), which then should be replaced. If, however, the pressure drops on closing stopcock 11 (with 9 open) then either the bulb has a leak, or offgassing from previous runs is occurring. Leaks can be checked using a Tesla coil. Such maintenance procedures should be routinely carried out on all portions of the vacuum gas handling system. This includes changing the rotary pump oil at frequent intervals.

B. Preparation of Methyl Nitrite

Methyl nitrite (CH_3ONO) is prepared by the dropwise addition of 50% H_2SO_4 to a solution of methanol (CH_3OH) saturated with $NaNO_2$. For the protocol described here, the use of ~50 cm^3 of each (50% H_2SO_4 and sodium nitrite saturated methanol) is sufficient. A schematic of the apparatus needed is shown in Figure 5 (Section II). A solution of methanol saturated with sodium nitrite is placed in the three-necked flask (300 mℓ volume) (A). The 50% H_2SO_4 is placed in the funnel (B) equipped with a Teflon stopcock. Ultra-high purity nitrogen is passed through the flask via inlet and outlet joints (C) and (D). Bubblers (E) and (F) contain a saturated NaOH solution and anhydrous $CaCl_2$, respectively, while trap (G) is fitted with high vacuum greaseless stopcocks (Kontes #K-826500 or equivalent) and the necessary ball and socket and "o"-ring joints, as shown. The system should be purged with a nitrogen flow for ~10 minutes prior to commencing the dropwise addition of H_2SO_4 into the $NaNO_2$ saturated CH_3OH. The trap (G) should be cooled to 196 K by means of a Dewar filled with a dry ice/acetone slush just prior to beginning the reaction. The CH_3ONO produced is swept out of the reaction vessel by the N_2 stream, any H_2SO_4 carried over is removed by passage through the NaOH solution, and the CH_3ONO-N_2 stream is then dried by passage through the

trap containing anhydrous $CaCl_2$. The CH_3ONO is collected in the cooled trap (G).

After the reaction has terminated, the N_2 flow is turned off, stopcocks 13 and 14 on the trap (G) are closed, and the trap, still cooled to dry ice/acetone temperature by the Dewar, is connected to the vacuum system (Figure 4) via the "o"-ring joint (E). The Dewar containing dry ice/acetone is then replaced by a Dewar containing liquid nitrogen.

After preparation of the methyl nitrite, as described above, the trap (G) is degassed by opening stopcocks 6 and 13, with the trap still immersed in liquid nitrogen. After pumping down to $<10^{-4}$ torr, stopcock 13 is closed, and the methyl nitrite can be stored indefinitely at liquid nitrogen temperatures under vacuum. The trap (G) and Dewar should be covered with an opaque cover (e.g., aluminum foil) in order to avoid photolysis of the methyl nitrite.

C. Experimental Procedure for the Determination of Rate Constants for Reaction with the Hydroxyl Radical

1. Filling the Reaction Bag

Prior to each new experiment, the reaction bag should be completely emptied using a metal bellows pump whose exhaust is expelled into a hood. The bag should then be filled with pure air and pumped out again to remove any test compound or other reactants or products from the previous run. The desired amounts of the reactants (i.e., methyl nitrite, NO, the test compound and the reference organic) are then introduced (see below, Section III.C.2), and the reaction bag is filled (i.e., visually filled but not excessively so as to cause undue stress on the seams) with ultra-zero air, using a flow rate in the range of ~7-10 liter min^{-1}, as monitored by the rotameter.

The reaction bag should be kept in the dark during the injection of the reactants, since methyl nitrite photolyzes rapidly.

2. Introduction of Initial Reactants

a. Injection of Methyl Nitrite

This protocol calls for introduction of 0-10 ppm of methyl nitrite into the reaction bag, depending on how rapidly this test organic (and reference compound) react. A convenient method of introducing CH_3ONO is to admit the desired pressure of CH_3ONO from the trap (G) into the ~500

cm^3 Pyrex bulb (K) by gradually warming the trap until the desired pressure is attained. The desired pressure, P, to introduce into the bulb is given by

$$p(\text{torr}) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{atmospheric pressure (torr)}] \times [\text{volume of reaction bag (liters)}]/[\text{volume of bulb } (cm^3)] \quad \text{(VIII)}$$

The volume of bulb (K) should be accurately measured by, for example, the volume of water it holds. For a 500 cm^3 bulb and a 75-liter reaction bag, 1.14 torr in the 500 cm^3 bulb corresponds to 10 ppm (at 760 torr) in the reaction bag.

The bulb (K) is first pumped down to $\lesssim 10^{-4}$ torr, then with stopcocks 5, 7 and 10 closed and stopcocks 6, 9, 11 and 13 open, the liquid nitrogen Dewar removed from trap (G), and the pressure is allowed to rise to the desired level, as read by the capacitance manometer (J). Stopcock 13 is then closed, the liquid nitrogen Dewar replaced around trap (G), and, after allowing the pressure to equilibrate, the pressure is read and stopcock 11 is closed. The high vacuum manifold, including trap (F), is evacuated, i.e. stopcocks 2, 3, 5, 7, 9, and 10 open, the rest closed. After evacuation to $\lesssim 10^{-4}$torr, stopcocks 5 and 10 are closed and nitrogen (of a stated purity level of $\gtrsim$99.99%) is introduced into the vacuum rack through the molecular sieve trap (F) to attain a pressure of ~10 torr. Stopcock 11 is then opened and the pressure of nitrogen increased to ~10 torr above the ambient atmospheric pressure. Stopcocks 8, 9 and 11 are then closed. The bulb (K) is then attached to the reaction bag as shown in Figure 7, stopcocks 11 and 12 are opened and the contents of bulb (K) flushed into the reaction bag by a monitored flow of ultra-zero air.

b. Injection of NO

This protocol requires the introduction of ~5 ppm of NO into the reaction bag. For NO (and other gaseous reactants which are commercially available in high pressure cylinders) this is most conveniently carried out using all-glass syringes as described below. The volume, V, of NO or other gaseous compound required to achieve the desired concentration in the reaction bag is given by:

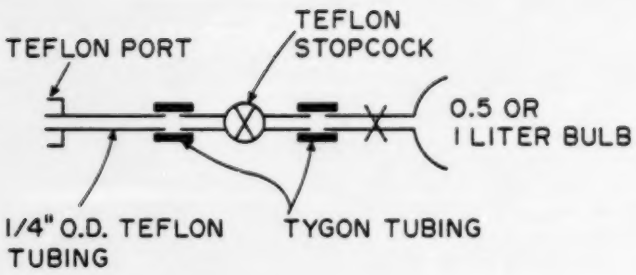


Figure 7. Attachment of Pyrex Bulbs to the Injection Port

$$V(cm^3) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{volume of reaction bag (liters)}] \quad \text{(IX)}$$

Using the reaction bag described in this protocol, approximately 0.375 cm^3 of gas are required to yield the desired concentration of 5 ppm in the bag. To obtain such a small volume of gas, pure NO from a high pressure cylinder is used to fill a 10-mℓ all-glass gas syringe (with the syringe being emptied and filled with NO several times to assure that dilution by air is minimized), 7.5 mℓ of NO is then transferred from the 10-mℓ syringe into a 100-mℓ all-glass gas syringe containing ~92.5 mℓ of pure N_2. N_2 rather than air must be used to dilute the NO to avoid its oxidation to NO_2, which will occur relatively rapidly when high concentrations of NO are mixed with O_2. For this transfer the two syringes are connected tip-to-tip by an ~0.4 in. long Tygon tube, as shown in Figure 8. The syringes are pumped back and forth a few times to ensure mixing. From this 100-mℓ syringe, 5.00 mℓ is then taken in the 10-mℓ syringe and injected into an ~1-liter bulb modified as shown (Figure 9), which as been pre-flushed with pure air for ≥5 minutes. The contents of this closed 1-liter bulb are then flushed into the reaction bag with pure air.

c. Injection of Test Compound and Reference Organic

Concentrations of the test compound and reference organic used in the development of this protocol have been in the range of 0.5 to 2 ppm by volume. The following protocol details the introduction of a compound to yield a concentration of ~1 ppm in the reaction bag. The specific technique employed depends on whether the compound is gaseous, liquid, or solid at room temperatures.

(1) Gaseous Compounds

If the test compound or reference organic is gaseous at room temperature, it can be injected either using a gas handling system as described above for methyl nitrite, or using all glass syringes as described above for NO. For most compounds, the latter technique is more convenient. If 1 ppm of the compound in the reaction bag is desired, then 1.00 mℓ of the diluted compound in the 100-mℓ syringe is injected into the ~1-liter bulb rather than the 5.00 mℓ as described above for NO. In addition, pure air rather than N_2 can be used as the diluent gas.

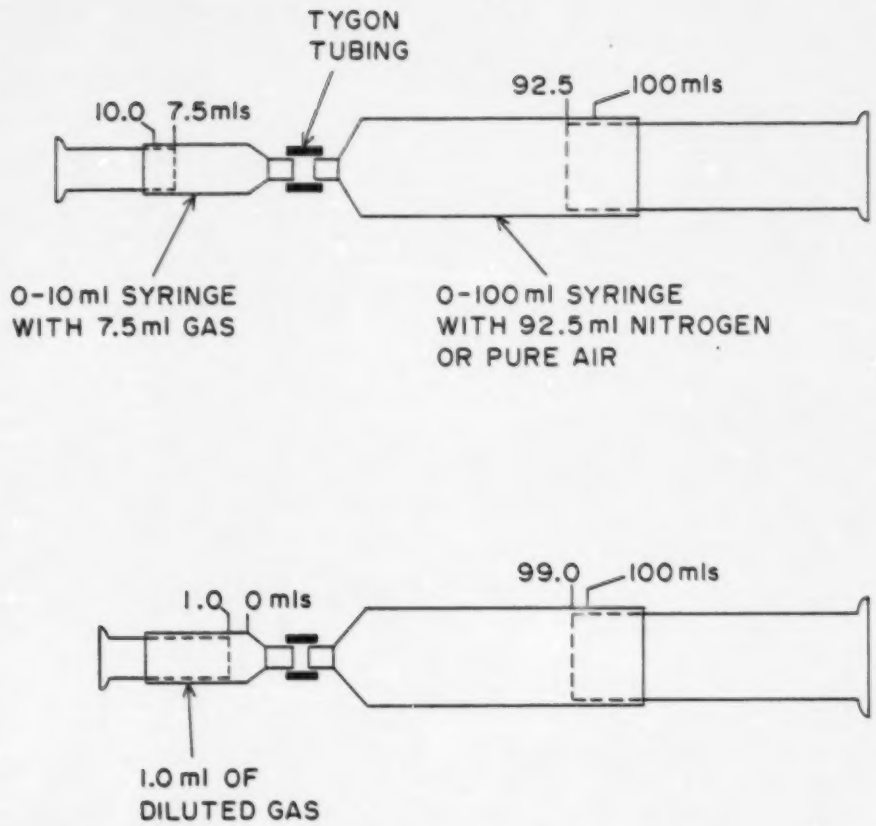


Figure 8. Syringe-to-Syringe Gas Transfer. (The volumes shown are for injection of 1 ppm of a gaseous compound into a 75-liter reaction vessel.)

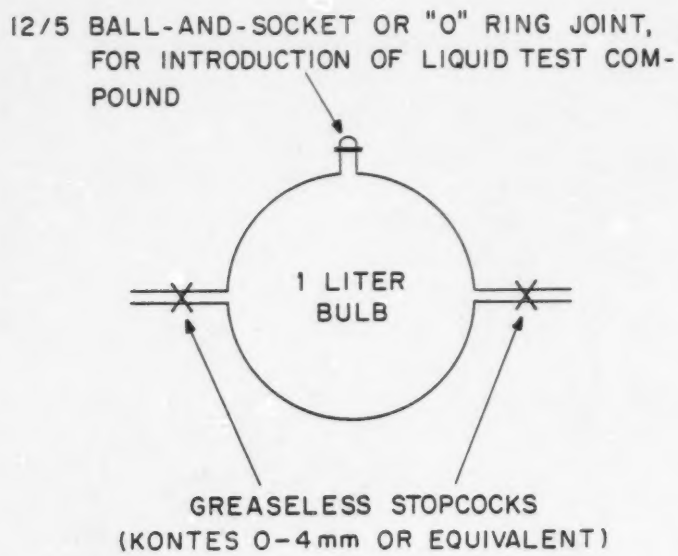


Figure 9. Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds

(2) Liquid Compounds

If the test compound or reference organic is a liquid, a different method of injection and of calculating the amount needed is necessary. For the reaction bag described in this protocol approximately 0.5 μl of liquid will give a concentration appropriate for an experiment aimed at an initial concentration of ~1 ppm, since for the liquid case:

$$V\ (\mu\ \text{liters}) = 10^{-4} \times [\text{desired concentration (ppm)}] \times \frac{[\text{Volume of bag (liters)}] \times [\text{Molecular Weight (g)}]}{[\text{Density (g cm}^{-3})] \times 2.46} \qquad (X)$$

at room temperature.

The calculated [see equation (X) above] amount of the liquid test compound is then injected into a 1-ℓ bulb, modified as shown in Figure 9, which has been preflushed with pure air into the hood for ≥5 minutes. The dosed 1-ℓ bulb is then attached to the reactor as shown in Figure 7 and its contents are then flushed into the bag with pure air at a known flow rate, which should be ~3.5 liter min^{-1} for a more volatile liquid or less (~1-2 liter min^{-1}) for a nonvolatile liquid. Evaporation of the lower volatility liquids may be aided by gentle use of a heat gun to warm the 1-liter bulb (taking care not to pyrolyze the compound). If heat must be applied, any tendency of a compound to air oxidize or polymerize will lead to low volatility residues and hence errors when carrying out liquid injections. The compounds should, if such problems are known to be likely, be first distilled by conventional means, i.e., vacuum distillation with liquid nitrogen trapping, vapor transfer from trap-to-trap at dry ice temperature, or by distillation at atmospheric or subatmospheric pressure and N_2 rather than air should be used as the flush gas.

(3) Solid Compounds

If the test or reference compound is a solid at room temperature, the desired mass (m) of compound to inject is given by

$$m(g) = \frac{10^{-7} \times [\text{desired concentration (ppm)}] \times [\text{volume of bag (liters)}] \times [\text{molecular weight (g)}]}{2.46} \qquad (XI)$$

If the compound has a melting point below ~50 C, is relatively volatile, and is known to be stable above its melting point, it can be injected in a manner analogous to that described above for liquids. In this procedure, the desired, weighed amount of compound is placed in the 1-liter bulb shown in Figure 9, which has been previously flushed with N_2, the bulb is attached to the reactor as shown in Figure 7, the compound is carefully heated with a heat gun until it melts, and then it is flushed into the reactor.

For solid compounds for which the above method is not suitable, an alternate technique must be employed. In this method, a 3 to 6-in. x 0.25-in. o.d. Pyrex tube is loosely packed with the compound, which is held in place with Pyrex wool. Tests should be carried out to assure that none of the solid compound is blown from the tube when air flows through it at ~2 liter min^{-1}. The tube is then attached to a simple dilution system as shown in Figure 10, which is in turn attached to the reactor. The compound is injected into the reactor by flushing the tube with ultrahigh purity air at a controlled rate in the range of 1-2 liter min^{-1} for the necessary amount of time to achieve the desired concentration in the reactor, with the diluent flow being at least a factor of 2 higher. The tube should not be heated. The diluent is necessary to avoid exposure of the injection inlet tube to the test organic at its vapor pressure, which may result in condensation. If the compound's vapor pressure at room temperature is known, the length of time to flush a desired quantity into the chamber is given by:

$$\text{time (min)} = \frac{10^{-6} \times [\text{desired concentration (ppm)}] \times [\text{volume of bag (liter)}]}{[\text{vapor pressure (atm.)}] \times [\text{flow rate (liter min}^{-1})]} \qquad \text{(XII)}$$

If the compound's vapor pressure is not known, the time required to obtain a given reactant concentration in a given volume at a given flow rate will need to be determined experimentally. To avoid contamination of the reactor, a different reaction bag should be used for these trial injections than used in the reactivity experiments, unless it is known that the amounts injected in the trials will be less than those required for the reactivity experiments. Ultrazero air should be used as both the flush and the diluent gas.

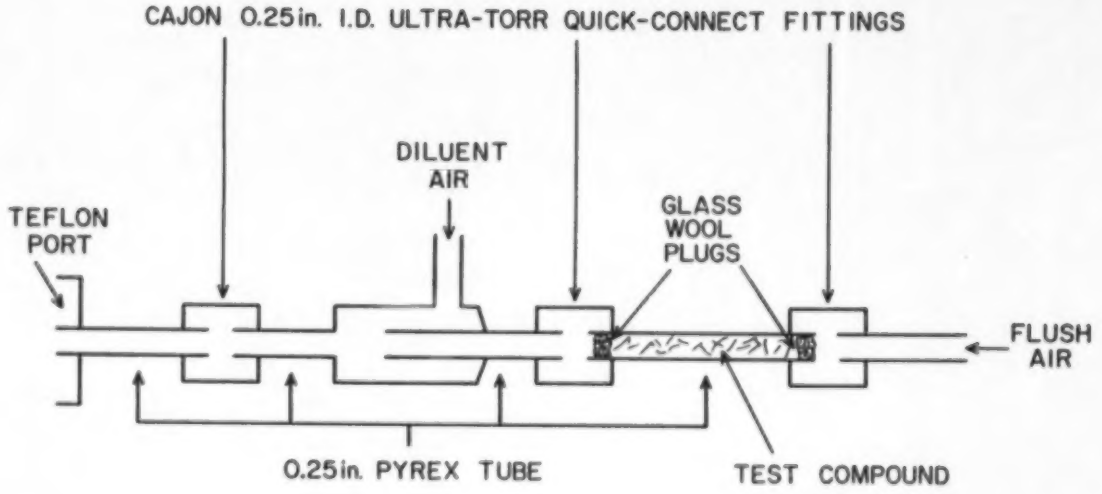


Figure 10. Apparatus for Introducing Solid Compounds into the Reaction Chamber

If the compound is relatively nonvolatile, the amount of air used to inject it may be comparable to the bag volume, so in these cases the reactor should be nearly empty prior to the injection of the organic. This protocol is not intended for use for compounds whose vapor pressure is less than ~10 ppm (~0.01 torr), since it would not be possible to use this technique to achieve concentrations of ~1-2 ppm in the reaction bag.

3. Pre-Irradiation Analyses

When the reactants have been injected in the reaction bag and mixed, the concentrations of the test compound and the reference organic are determined. The discussion in this and in the following section is based on gas chromatography being employed for the analysis of these species. Analogous considerations apply if other analytical techniques are employed.

Samples for analyses by gas chromatography are conveniently taken by a 100-mℓ all-glass, gas-tight syringe. The syringe is flushed by withdrawing and expelling 100 mℓ of the gas to be sampled two or three times prior to taking the sample for analysis. While the data analysis does not strictly require absolute concentrations [equations (V) and (VI) in Section I involve only relative concentrations], the gas chromatograph(s) should, if possible, be calibrated for the test compound and reference organic. A minimum of three gas chromatographic samples should be analyzed prior to turning on the lamps.

Based upon literature results, the reproducibility of these analyses will depend on the particular organic compounds being studied. A reproducibility of ±2% should be aimed at, and this can be achieved for the $\lesssim C_9$ alkanes and the smaller alkenes. For other classes of compounds, such as organics of low volatility or organics which tend to be adsorbed on the reaction walls, an analytical reproducibility of only ±5% may be achievable. The minimum rate constant measurable with this protocol is directly related to this analytical reproducibility. Thus with a reproducibility of ±2%, the lowest rate constants which can be measured will be ~3×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. For lower analytical reproducibilities, only higher rate constants can be measured. Clearly, for fast reacting organics with rate constants $\gtrsim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}, an analytical reproducibility of ~±5% is adequate.

If the first two analyses agree to within the necessary reproducibility, then immediately after the third sample is taken from the reaction bag, the lamps can be turned on. If the first two analyses disagree by more than the expected reproducibility, then further samples should be taken until duplicate analyses are reproducible. In between gas chromatographic sampling, the NO-NO_x and O_3 monitors should be sampling from the reaction bag, and their outputs displayed on stripchart recorders. Before beginning monitoring from the bag, these analyzers should be allowed to warm up according to the manufacturer's specifications. Teflon sampling lines (1/4 in. o.d.) should be used between the bag and the O_3 and NO-NO_x monitors in order to avoid losses experienced with, for example, Tygon or nylon tubing. The first three to five minutes sampling should be neglected since initial flushing of the sample lines is needed.

4. Irradiation Procedure

When stable concentration readings have been established (see above), the desired number of lamps are turned on, together with the cooling fan. The temperature beside the reaction bag should be monitored during the irradiation. Samples are taken for analysis as often as possible. If gas chromatography is employed for these analyses, this is constrained by the retention times of the test compound and the reference organic. O_3 and NO-NO_x monitoring should be carried out between sampling. Sampling for gas chromatographic analysis of the test compound and the reference organic must be carried out simultaneously.

With the protocol developed here, the irradiation should be terminated, and the last analytical samples taken, after ~30 minutes for full light intensity, ~45 minutes for two-thirds maximum light intensity or ~60-90 minutes for one-third maximum light intensity. Since it is preferable to have two to four analyses during the irradiation, the optimum light intensity is then determined by the gas chromatographic retention times. As an example, Figure 11 shows a typical set of gas chromatograms for an n-butane + propene system, for which analyses were carried out every 15 minutes during the 45 min irradiation. In Figure 12, an example of the OH radical concentration as a function of time, derived from such analyses, is shown.

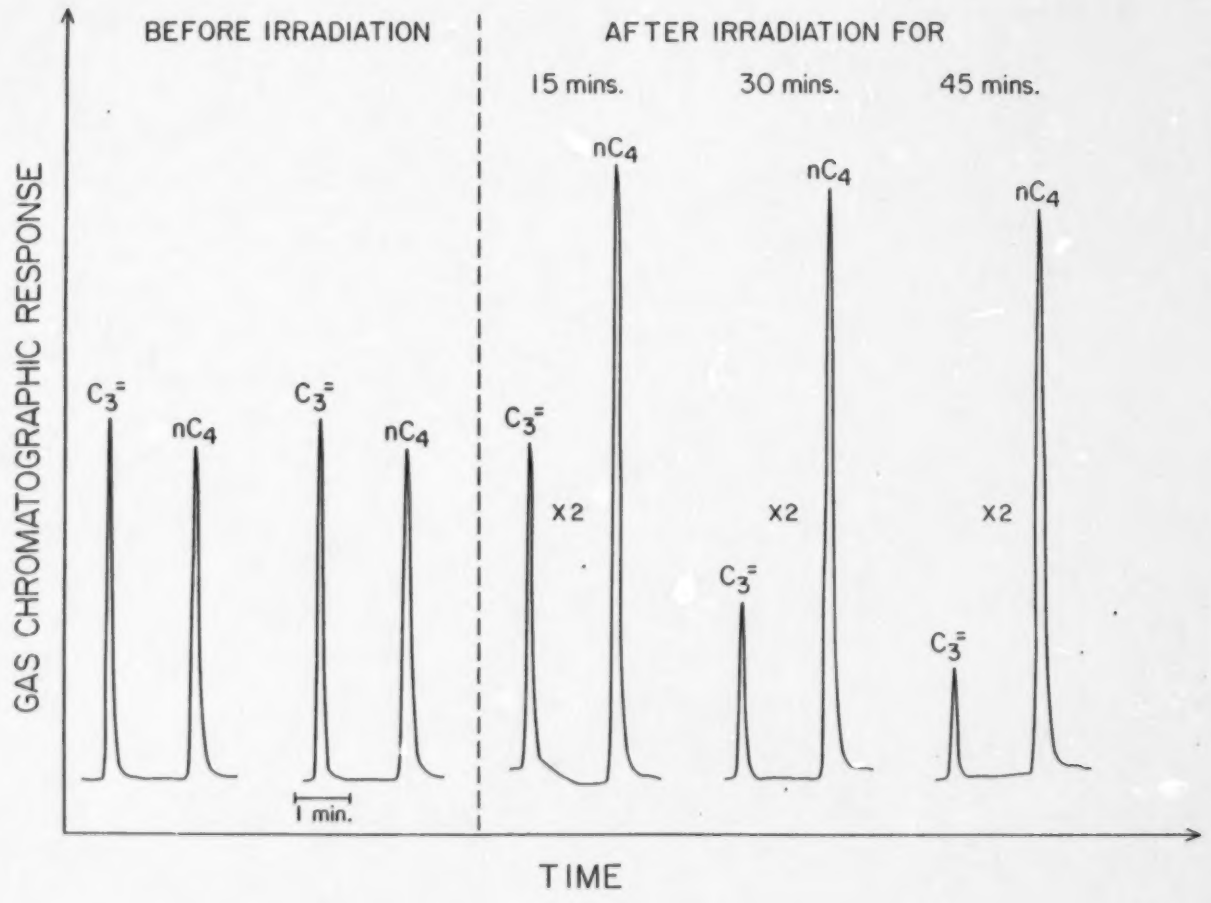


Figure 11. Example of Gas Chromatographic Analysis of Propene ($C_3^=$) and n-Butane (n-C_4) During a CH_3ONO/NO/Propene/n-Butane/Air Irradiation

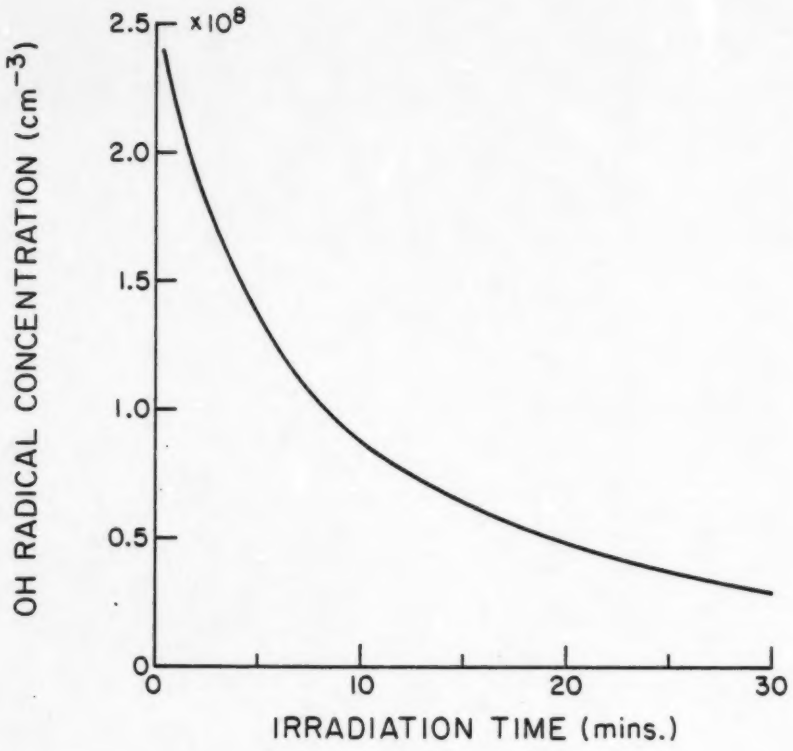


Figure 12. OH Radical Concentrations During a Typical Irradiation at Full Light Intensity with an Initial Concentration of CH_3ONO of 10 ppm

For compounds which are suspected of reacting rapidly with OH radicals, the irradiations should be carried out with one-third light intensity and low (~4 ppm) concentrations of CH_3ONO, with short irradiation times ($\lesssim$5 minutes). In this case, only one analysis will probably be able to be carried out for each irradiation, and a larger number of irradiations will be necessary (See, for example, Atkinson and Aschmann 1984).

For organics which exhibit an absorption spectrum in the actinic region with a significant photolysis rate (Pitts et al. 1981), at least three sets of irradiations should be carried out, with CH_3ONO concentrations of 0, ~5 ppm and ~15 ppm. Three concentrations are necessary because the origin cannot be used as a point in plots of equation (V). For organics which do not photolyze, at least two sets of irradiations should be carried out with CH_3ONO concentrations of ~5 and ~10 ppm.

5. Safety Considerations

Full safety precautions consistent with the known or unknown toxic, mutagenic or carcinogenic hazards of the test compounds must be taken. If the test compound is known to be hazardous or toxic, or if there is a reason to believe that it is, then handling should be carried out in a hood with disposable gloves, and if the compound is a liquid it should be measured using a variable micropipette with disposable tips. Used gloves and tips should be disposed of according to safety regulations. If the toxicity of a liquid compound is not a problem, a 10 $\mu\ell$ capacity Hamilton liquid syringe may be used, but it should be cleaned immediately after use by alternately drawing in and expelling methanol or some other appropriate solvent five to ten times and then completely drying it by flowing dry nitrogen or pure air through the body of the syringe. Similar precautions should be taken with hazardous or toxic gases or solids. Obviously, if the hazards or toxicological characteristics of a compound are not known, then the compounds should be treated as if they are known to be hazardous or toxic.

D. Data Analysis

The concentrations of the test compound and reference organic, as determined by gas chromatography or some other suitable analytical

technique, are used to plot equation (V). An example of a plot of equation (V) is shown in Figure 13 for irradiations of three hydrocarbons and ethane. Least squares analyses of the slopes of these plots yield the rate constants ratios k_1/k_2. The intercept with these compounds is zero since they do not photodissociate, but an intercept is observed if the compound photodissociates or undergoes a light-induced wall loss.

The rate constant, k_1, can then be calculated from the slope of equation (V) and the known value of k_2, the rate constant for the reference compound. This rate constant can then be used to classify the atmospheric reactivity of the test compound. In particular, its rate constant can be compared with those for other organics to determine where it fits relative to those on the reactivity scale. For example, if it is determined that compounds which react slower than ethane can be considered to be unreactive, then if the value of k_1 so determined is less than 2.75×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, the OH rate constant for ethane (Atkinson, 1985), then the test compound can be considered to be unreactive by this criterion.

E. Reference Organics

These organics are chosen for ease of analyses and must have accurately known OH radical rate constants. They should not photolyze and, preferably, they should not react with O_3 or NO_3 radicals. If the reference compound does react with O_3 or NO_3 radicals, care should be taken to assure that sufficiently high levels of NO are present during the experimental runs to suppress the levels of these species. In addition, the OH radical rate constant for the reference compound should be similar to that for the test compound, preferably to within a factor of two to three. Table 1 gives a list of recommended reference organics, together with their OH radical reaction rate constants at room temperature.

F. Information to Be Reported

A report of the results should include for each test compound the following:

a. The compound's name, formula and physical properties (boiling and melting points).

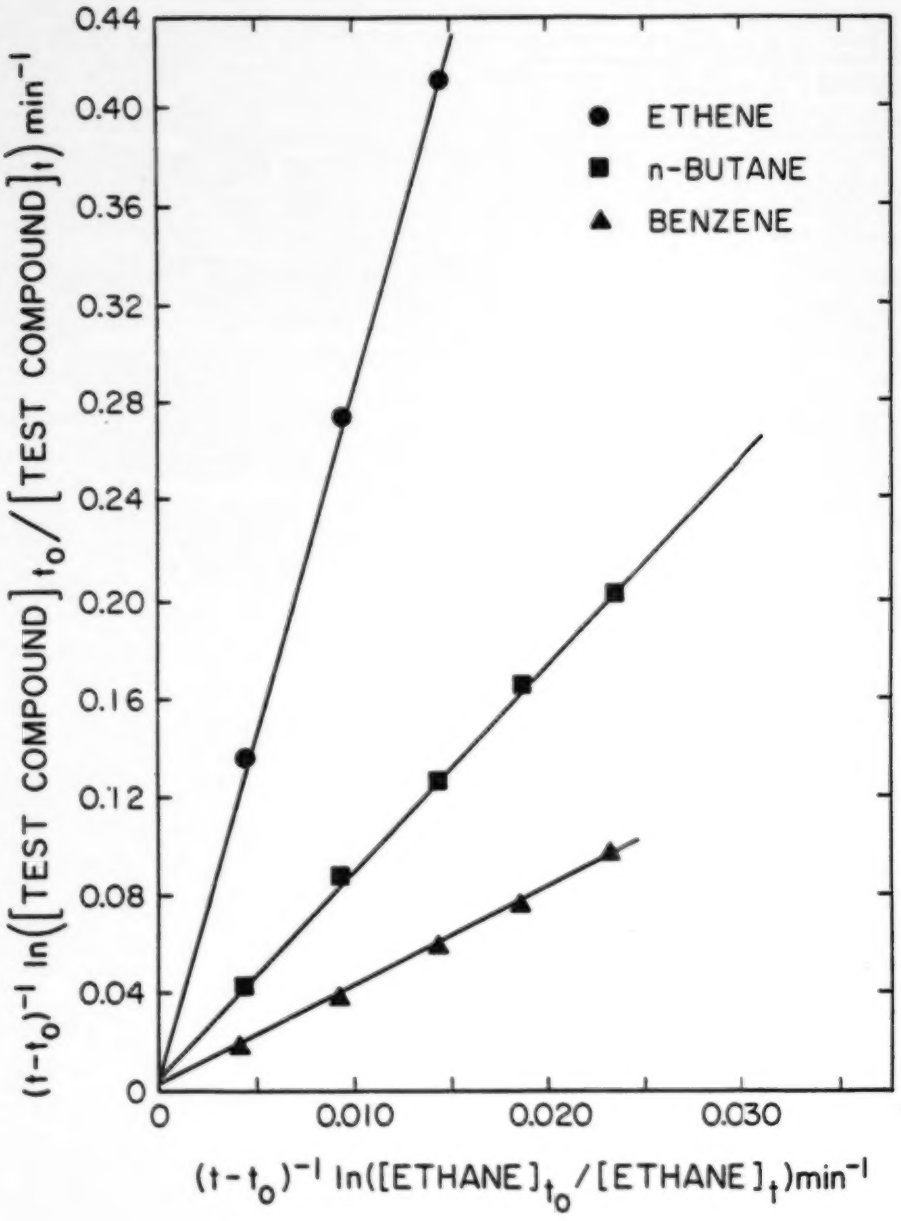


Figure 13. Plot of Equation (V) for Several Hydrocarbons Using Ethane as the Reference Organic

Table 1. List of Several Organics for Which Accurate OH Radical Rate Constants are Available, and Which do not Photolyze

Organic	$10^{12} \times k^{OH}$ (cm^3 $molecule^{-1}$ sec^{-1})[a]
Ethane	0.28
n-Butane	2.5
Cyclohexane	7.4
Ethene[b]	8.5
Propene[b]	26
2-Methyl-2-butene[b]	87
Isoprene[b]	100

[a] At 298 K, from Atkinson (1985).
[b] These compounds react with O_3 (Atkinson and Carter 1984) and are not suitable as reference compounds unless NO is in large excess of O_3. (This is generally true with short reaction times when excess NO is added.)

b. The chemical's physical form used during injection (gas or liquid at room temperature), method of purification and purity including analysis of impurities).

c. The temperature during each run.

d. The name and formula of the reference organic used and the rate constant, k_2, used in the data analysis.

e. The initial concentrations of the reference organic and test compound, NO and CH_3ONO.

f. An indication of the analytical technique(s) employed for the test and reference compounds.

g. The data obtained (i.e., the concentrations of the reference organic and test compound prior to and during irradiation, and the values of $(t-t_o)^{-1}$ $\ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ and $(t-t_o)^{-1}$ $\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$.

h. Plots of equation (V) or, if the test compound does not photolyze, equation (VI).

i. The value of k_1/k_2 and hence of k_1 determined by least squares analysis from such a plot.

j. A discussion of any special problems encountered in the experiments employing the test compound, or any special procedures which had to be employed, and the results of any experimental tests which might reflect on the accuracy of the value of k_1 obtained.

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